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SPECIFICATION

1. Title of Invention

Catalyst for Cleansing of Exhaust Gas

2. Claim

Catalyst for the purpose of rendering innocuous the contents of exhaust from internal combustion engine, such as hydrocarbons, carbon monoxide and nitrogen oxide, the catalyst consisting of catalytic layer No. 1 of which zeolite is the main component, and catalytic layer No. 2 of which the main component is a noble metal, catalytic layer No. 1 being overlain with catalytic layer No. 2 and the preparation then being borne on a carrier.

3. Detailed Description of the Invention

[Industrial Utility]

This invention concerns a catalyst for cleansing the exhaust from internal combustion engines, specifically a catalyst called tertiary catalyst.

A ternary catalyst is a substance for installation in the exhaust system of internal combustion engine of an automobile for the purpose of rendering innocuous the 3 components of the exhaust gas, namely hydrocarbon, carbon monoxide and nitrogen oxide, the oxidative and reductive components of the catalyst being virtually in equal amounts stoichiometrically.

[Existing Technology]

The principal type of catalyst in use today for cleansing the exhaust gas from internal combustion engine is the so-called ternary catalyst which performs oxidation and reduction simultaneously with equal efficacy. The ternary catalyst may consist, for instance, of noble metals such as platinum (Pt), palladium (Pd) and rhodium (Rh) carried on a monolith carrier having a honeycomb cross section. For the monolith carrier, material such as Kogelite which has a small coefficient of thermal expansion and high heat resistance. The carrier is then coated with

a porous (large surface area) material such as activated alumina or zirconia, after which it is charged with a noble metal catalyst. A specific example of a ternary catalyst carrying noble metals is a Pt-Pd-Rh preparation described in Japanese Patent Publication S57-20013. In that example, Pd which is subject to loss of performance through poisoning is placed inside and Pt and Ir are placed in the outer layers.

This type of ternary catalyst exhibits its high oxidation-reduction activity in the vicinity of the theoretically optimum A/F ratio, and therefore the exhaust which is brought into contact with the catalyst should be close as possible to the theoretical A/F ratio. This control is carried out according to the oxygen concentration in the exhaust detectable by a senser provided upstream to the catalyst. In practice, the theoretical A/F ratio is attained by adjusting the amount of fuel fed to the internal combustion engine, and amount of air suction and the amount of air fed into the exhaust in accordance with the oxygen concentration in the exhaust upstream to the catalyst.

[Problem Which This Invention Purports to Solve]

When the internal combustion engine of a car is started cold, the A/F ratio decreases (the atmosphere is enriched) since the amount of fuel fed to the engine is increased. Not only do the amounts of carbon monoxide and hydrocarbon in the exhaust increase but, since the temperature is low, the ternary catalyst does not function adequately , and removal of CO and HC is especially affected.

The objective of this invention is to present a ternary catalyst which shows high activity for cleansing Exhausts especially of hydrocarbons while the engine is still cold and the A/F is in the enriched state.

[Method for Solving the Existing Problem]

The catalyst of our invention is characterized by having two catalytic layers with zeolite as the intermediate layer, i.e., a ternary structure.

Specifically the design of this invention is as follows (with reference to the illustration;.the numbers cited refer to the symbols used in the diagram).

The catalyst of our invention is provided for the purpose of rendering innocuous the hydrocarbons, carbon monoxide and nitrogen oxide in exhaust gas from internal combustion engines. This catalyst is obtained by overlaying a carrier (10) with catalyst layer No. 1 (12) of which zeolite is the main component, this layer No. 1 then being overlain with catalytic layer No. 2 (14) which is oxidative-reductive and has as its main component a noble metal type catalyst.

In this structure, the carrier is a single-mass or the so-called monolith type. It may consist of pellets. The material may be a ceramic such as codelite or a laminate of heat-resistant metal sheets. The pellet type may consist of alumina pellets.

Catalyst layer No. 1 is a porous layer of which the main component is zeolite. Zeolites have chemical compositions similar to those of feldspars and are represented by the formula WnZnO2n.ILLEGIBLE H2O (in which W may be Na, Ca, K, Ba or Sr, Z is Si+Al and Si/Al > 1). The internal structure of zeolite consists of basket-like hollows and tunnel-like paths of varying diameter which connect these hollows. These spaces confer zeolite with ion exchange, adsorptive, molecular sieve and catalytic properties. Catalyst layer No. 1 may contain, in addition to zeolite, heat-resistant oxides such as alumina, zirconia and rare earth oxides.

This layer may also carry noble metal catalysts of Pt, Pd, Rh, etc. In addition, it may also carry rare earth oxides such as ceria (CeO_2) or lantana (La_2O_3). PN TM

Catalyst layer No. 2 is formed by coating catalyst layer No. 1 with alumina, etc., and charging this coating with noble metal catalyst of Pt, Pd, Rh, etc., in the form of solution. One or more noble metal may be used. The amount of noble metal should be 0.1-10 g per liter carrier. When the amount is less than 0.1 g/l there is little effect of the ternary catalyst, and when the amount exceeds 10 g/l the catalytic effect is not commensurate with the cost. The coating may contain rare earth oxide such as CeO_2 or La_2O_3 or zirconium oxide. The heat-resistance of catalyst layer No. 2 is thereby increased. When CeO_2 is used, its capacity for oxygen storage makes it possible to widen the window (spread of A/F ratio for maintaining the cleansing capacity of thrnary catalyst) of the catalyst.

This catalyst is maximally effective in the exhaust temperature range of 300-800°C, during which the space velocity (SV) of the flow of the exhaust should be 10,000-12,000 hr^{-1}.

[Mode of Action]

By using the catalyst of our invention, hydrocarbon is selectively adsorbed by catalyst No. 1 (12), the intermediate layer, while the engine is still cool and the gas mixture is enriched. As result, HC in the exhaust is diminished. As the engine warms, the temperature of the exhaust rises to warm the catalyst, and HC is gradually detached from zeolite in catalyst layer No. 1, and HC and CO are oxidized at the catalyst layer No. 2 (14) which has been activated, while NO_x is reduced and rendered innocuous.

[Examples]

Examples and Controls to explain this invention are now described with reference to Fig. 1.

Fig. 1 shows a portion of a cross section of a monolith catalyst. Fig. 2 shows the relation of the temperature of incoming gas to HC cleansing in Examples a and 2 and Controls 1, 2 and 3. Fig. 3 shows the same relationships for Examples 3, 4 and 5 and Control 4.

Example 1

The carrier was a cordelite honeycomb of the monolith type (10 in Fig. 1). It contained 400 cells of square cross section per square inch of the carrier cross section with an apparent volume of 1.3 liters. It was pretreated with water and then immersed in a wash coat slurry. The spurry was prepared by mixing 100 wt parts zeolite and 80 wt parts silicasol with water and nitric acid. The monolith was then removed from the slurry and excess spurry was blown off by a blast of compressed air. The carrier was then dried at 200°C to remove free water and then calcined at 700°C for 1 hour. The product was monolith carrier 10 coated with zeolite (catalyst layer No. 1, 12) of about 25 µm thickness.

This monolith carrier 10 bearing zeolite coat layer 12 was pretreated with water and then immersed in a wash coat slurry of mostly alumina. Excess slurry was blown off as described for zeolite layer 12 and the preparation was dried to obtain an alumina coating of about 25 µm thickness. This wash coat slurry was obtained by mixing 100 wt parts alumina and 14 wt parts aluminum nitrate solution with water and nitric acid in a ball mill.

The alumina coating layer was charged with Pt, Rh, La and Ce by conventional technique to obtain catalyst layer No. 2 (14). The amounts of the ingredients were 1.5 g Pt, 0.3 g Rh, 0.03 mol La and 0.3 mol Ce per liter carrier.

Example 2

The procedure in Example 1 was followed except for making the thickness of the zeolite layer (catalyst layer No. 1) 10 µm.

Control 1

Catalyst layer No. 2 was not formed, and the thickness of the zeolite (catalyst layer No. 1) layer was about 50 µm.

Control 2

Zeolite (catalyst layer No. 1) layer was not formed and the thickness of the catalyst layer No. 2 was made 50 µm.

Control 3

In this preparation, the noble metal catalyst layer of Example 1 was applied to monolith as catalyst layer No. 1 and zeolite layer was placed above it as catalyst layer No. 2.

Results of Evaluation 1

The cleansing performances of Examples 1 and 2 and Controls 1, 2 and 3 were measured and evaluated.

Each catalyst was set in the exhaust system of a 4-cylinder engine (exhaust volume 1.6 l) and studied for activity. The temperature of the incoming gas was varied from 100°C to 500°C and HC cleansing was measured. The A/F was set at 13.5

(fuel excess or "rich burn") and the space velocity (SV) of the exhaust gas was about 60,000 hr^{-1}.

It may be seen from Fig. 2 that the catalysts in Examples 1 and 2 which were based on our invention showed an extremely high level of removal of HC starting at low (100-200°C) temperature in a condition of fuel excess. indicating high activity at low temperatures. As the temperature of the incoming gas rose, there was a decrease in the cleansing performance, but activity was again high at high temperatures. The tentative lowering of cleansing efficiency as the temperature shifts from low to high may be attributed to some delay in the activation of oxidation in the interval from 200°C to HC detachment, but the interval is short and does not constitute a problem.

Example 3

As indicated in Fig. 1, a codelite honeycomb monolith carrier 10 was used as carrier. It had 400 cells of square cross section per square inch of carrier cross section, with the apparent volume being 1.3 l. It was pretreated with water and then immersed in wash coat slurry which consisted of 100 wt parts zeolite and 80 wt parts silicasol mixed by ball milling with water and nitric acid. The monolith was taken out of the slurry and, after the excess slurry had been blown off with compressed air, it was dried at 200°C to remove free water and calcined at 700°C for 1 hour. In this manner, monolith carrier 10 coated with zeolite (layer No. 1) of about 25 µm thickness was obtained.

The preparation was pretreated with water and then immersed in an aqueous solution of platinum dinitrodiamine and left there for 24 hours to achieve ion-exchange of 0.75 g Pt per liter carrier.

Thereafter, excess moisture was blown off, the preparation was dried for 1 hour at 250°C, and left immersed in a solution of rhosium chloride for 24 hours to attain an ion exchange of 0.15 g Rh per liter carrier, forming catalyst layer No. 1 (12).

Next the monolith carrier was immersed in a wash coat slurry of mostly alumina, and excess alumina was blown away as in the formation of the zeolite coating to form an alumina coating (layer No. 2). This alumina slurry was obtained by mixing 100 wt parts alumina and 14 wt parts aluminum nitrate solution with water and nitric acid in a ball mill.

The alumina coating was charged with Pt and Rh by conventional technique to obtain catalyst layer No. 2 (14). The amounts were 0.75 g Pt and 0.15 g Rh per liter carrier.

The total amounts of nobel metals carried in catalyst layers No. 1 and 2 were 1.5 g Pt and 0.3 g Rh per liter carrier.

The carrier was then immersed in a ceria solution, after which excess CeO_2 was blown off and the preparation was dried to obtain a material carrying 0.3 mol Ce per 1 carrier.

Example 4

The procedure in Example 3 was followed except for using Pd in place of Pt.

Example 5

The procedure in Example 3 was followed except for omitting the Ce.

Control 4

The procedure in Example 3 was followed but with the omission of catalyst layer No. 1, setting the thickness of catalyst layer No. 2 at about 50 µm, and using 1.5 g Pt, 0.3 g Rh and 0.3 mol Ce.

Results of Evaluation 2

The cleansing performances of Examples 3, 4 and 5 and Control 4 were measured and evaluated.

Each catalyst was set in the exhaust system of a 4-cylinder engine (exhaust volume 1.6 l) and studied for activity. The temperature of the incoming gas was varied from 100°C to 500°C and HC cleansing was measured. The A/F was set at 13.5 (fuel excess or "rich burn") and the space velocity (SV) was about 60,000 hr^{-1}.

It may be seen from Fig. 3 that the catalysts in Examples 3-5 based on our invention showed an extremely high level of removal of HC at low (100-200°C) temperature in a condition of fuel excess, indicating high activity at low temperature.

As the temperature of the incoming gas rose there was a decrease in the cleansing performance, but activity was again high at higher temperatures for HC, CO and NO_x. The tentative lowering of cleansing efficiency as the temperature rose above 200°C and HC removal began may be attributed to some delay in activation, but the interval was short and did not constitute a problem.

Efficacy of cleansing CO was compared at two temperature levels (150°C and 400°C) of incoming gas. With Control 4 they were 0% and 86%, respectively while with Example 3 they were 43% and 87%; with Example 4 they were 40% and 85% and with Example 5 they were 10% and 85%, showing that with Examples 3-5 the activity for removing CO at low temperature was also increased.

In Examples 3 and 4 to which a rare earth oxide was added, the O_2 storage effect resulted in oxidation in which HC was converted to CO_2 and thereby made innocuous. Moreover the heat of reaction accelerated the catalytic reaction so that activity at low temperature was greater than in Example 5.

The above examples demonstrate the specific effects of our invention, although it should not be construed that these examples define the limits of the invention. The scope of our claim encompasses a number of modifications.

[Efficacy of the Invention]

In the preparation of our invention, two catalytic layers are provided with an inner layer of zeolite, forming a ternary catalyst which exhibits high cleansing activity for hydrocarbons even at low engine temperature in a fuel-rich atmosphere.

The catalytic preparation of our invention is also characterized by the fact that when HC in the exhaust is increased with increased consumption of fuel under acceleration, HC is adsorbed by zeolite and temporary increase in HC is avoided.

4. Brief Explanation of the Illustrations

Figs. 1-3 provide explanations of the examples used to show the action of the catalyst according to our invention.

Fig. 1 is a diagram of a partial cross section of our monolith catalyst. Fig. 2 shows graphs which compare the relation of gas temperature to HC cleansing in Examples 1-2 and that in Controls 1-3. Fig. 3 is a similar comparison of Examples 3-5 with Control 4.

In Fig. 1, 10 is carrier, 12 is catalyst layer No. 1 and 14 is catalyst layer No. 2.

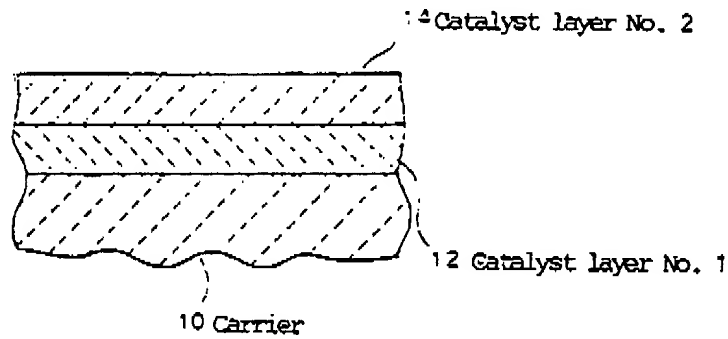

Fig. 1

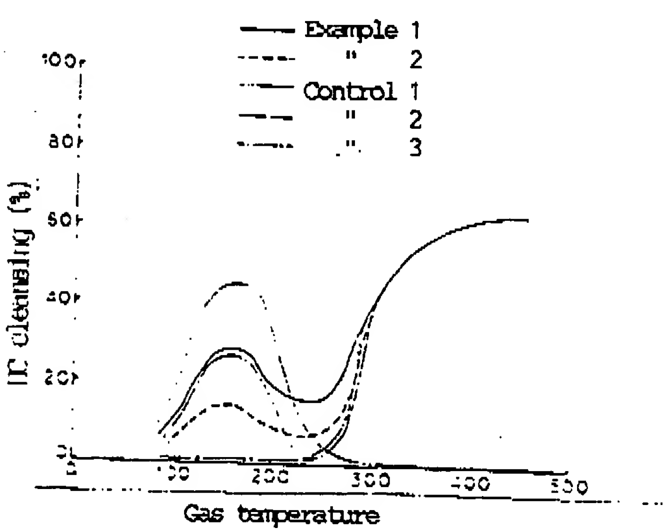

Fig. 2

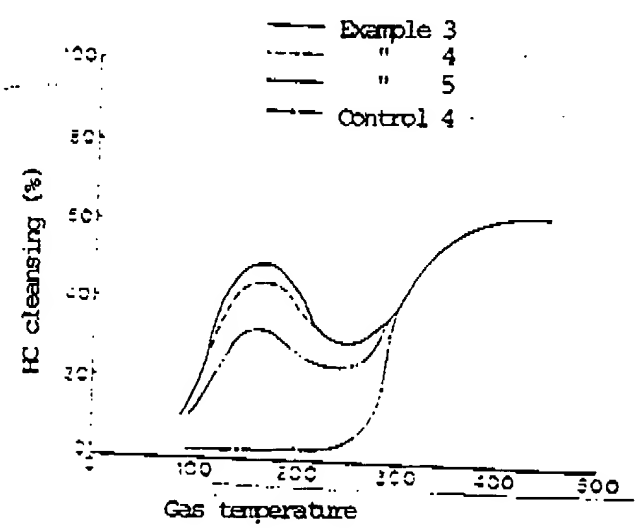

Fig. 3